NUCLEAR MAGNETIC RELAXATIONS AND MOLECULAR REORIENTATION FREQUENCIES OF α-HYDROQUINONE AND γ-HYDROQUINONE

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ABSTRACT. The spin-lattice nuclear magnetic relaxations have been measured for stable (α) and meta-stable (γ) Hydroquinones or Quinols. The studies were carried out as a function of temperature from 94°K to 360°K at the radio frequency of 25 Mc/sec. The N.M.R. relaxations show the molecular rotation with the rise of temperature in both the cases. The activation energies and molecular reorientation frequencies have also been calculated.

INTRODUCTION

The present work is an attempt to extend the work of Gupta (1963) on motion of α-Hydroquinone and γ-Hydroquinone molecules. His results of α--Hydroquinone for line-widths vs. temperature show first transition at about 341°K and second transition at about 388°K, with the specific heat anomaly which occurs at 325°K. In the case of γ-Hydroquinone first transition is found at about 365°K and second transition at about 375°K, with the heat anomalies occurring at temperatures 230°K and 336°K. These transitions are interpreted by him as being a reorientation of molecule about the molecular axis. The interchange of energy between nuclei and lattice may also be studied by means of spin-lattice relaxation time. The present N.M.R. relaxation measurements have been made on α-Hydroquinone and γ-Hydroquinone in an attempt to obtain more detailed informations concerning the nature of molecular motions.

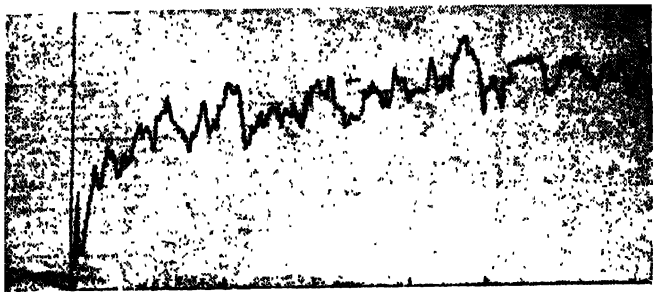
EXPERIMENTAL ARRANGEMENT

The magnetic relaxations of solid α-Hydroquinone and γ-Hydroquinone have been measured at 25 Mc/sec using a proton resonance spectrometer in a field of about 5998 gauss. The records of T_1 have been recorded by one of us in University College of North Wales, Bangor, U. K. The records of T_1 at room temperature have been shown in fig. (1) and fig. (2).

THEORY

Bloembergen *et al* (1948) derived an expression for T_1 in terms of a correlation time τ_c, which sets a time scale to the random motion. , can be roughly defined

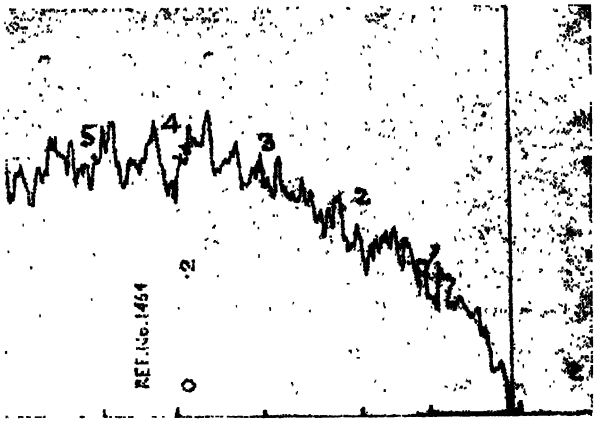
as the time taken by a molecule to turn through a radian or to move through a distance comparable with its dimensions.



0 60 120 180 240

Time in Seconds →

Fig. (1) Signal decay curve of T_1 for α-Hydroquinone at room temperature.



240 180 120 60 0

←Time in Seconds

Fig. (2) Signal decay curve of T_1 for γ-Hydroquinone at room temperature.

The expression has been slightly modified by Kubo and Tomita (1954) and obtained :

$$\frac{I}{T_1} = C_1 \left[\frac{\tau_c}{I+\omega_0^2\tau_c^2} \; \frac{4\tau_c}{I+4\omega_0^2\tau_c^2} \right]$$

where $\omega_0 = 2\pi\nu_0$ and C_1 is a constant.

Thus T_1 decreases as the value of τ_c increases, it reaches minimum when reorientation frequency and radio frequency become roughly equal, beyond which T_1 rises with temperature, such behaviour has in fact been found for three isotopic species of benzene by Andrew and Eades (1953b). With the help of above equation,

the values of T_1 at various temperatures can be converted in terms of τ_c. The plot of log τ_c vs $1/T$ yields a straight line and its slope will give the activation energy E_R. This procedure is the only approach when the plot of T_1 against $1/T$ gives no minimum value of T_1 due to the intervention of solid-solid phase transition as in the case of Cyclohexane (Andrew and Eades, 1953a).

METHOD FOR MEASUREMENT OF T_1

In the present work for the measurements of relaxation times Linder's (1957) decay technique has been adopted. Measurement by this method is possible when T_1 is long compared to the constant of the recording apparatus. The principle of the method is that when spin system is saturated by the application of the radio-frequency amplitude H_1, such that $\gamma^2 H_1^2 T_1 T_2$ is much greater than unity, the observed intensity falls until the signal vanishes completely. The radio-frequency field is lowered to the unsaturated value of nuclear system and regrowth of signal is recorded. The growth is exponential and governed by the formula :

$$S(t) = S_0\left(1-\exp\left(-\frac{t}{T_1}\right)\right)$$

where $S(t)$ and S_0 are the intensities of signals in saturated and unsaturated states. The slope of the curve $s_0-s_{(t)}$ against time (t) gives relaxation time T_1.

ACTIVATION ENERGY AND ROTATIONAL-FREQUENCY

Gutowsky and Pake (1950) and Kubo and Tomita (1954) modified the theory of Bloembergen *et al* and modified expression is given as :

$$2\pi\nu_c = \alpha\gamma\delta H\,[\,\tan\{\pi(\delta H^2-B^2)/2(C^2-B^2)\}]^{-1}$$

where ν_c is the correlation frequency for motion narrowing the line, C is the linewidth at temperature below the transition region, δH is the linewidth in the Transition region, B is the line width at higher temperature, γ is the gyromagnetic ratio and α is $(\text{aln}2)^{-1}$ and its value is $(8\times 0.6931)^{-1}$. (C^2-B^2) can be replaced by (C^2) if B^2 is too small as compared to C^2. The correlation frequency ν_c is assumed to obey Arrhenius equation :

$$\nu_c = \nu_0 \exp\left[\frac{-E_R}{RT}\right]$$

where E_R is the activation energy and R is the gas constant/mole.

In the case of α-Hydroquinone the value of C is 09.53 gauss and value of B is 0.31 gauss. In γ-Hydroquinone the value of C and B are 8.40 gauss and 0.40 gauss respectively. These values have been calculated with experimental linewidth vs temperature curve obtained by Gupta (1963).

The molecular reorientation frequencies for α Hydroquinne have been shown in Table II and for γ-Hydroquinone in Table III. The plot of log ν_c *vs* $1/T$ yields a straight line and its slope will give activation energy E_R for molecular rotation.

RESULTS

The spin-lattice relaxation times measured by signal decay method for α-Hydroquinone and γ-Hydroquinone are quoted in Table I.

TABLE I

Spin-lattice relaxation times of stable and *m*-stable Hydroquinone

Temperature °K	Stable Hydroquinone	*m*-stable Hydroquinone
94°	5.0 minutes	1.20 minutes
293°	3.0 ,,	0.90 ,,
353°	—	0.83 ,,
360°	1.4 ,,	—

TABLE II

Molecular reorientation frequencies for stable (α) Hydorquinone

Temperature °K	δ H (gauss)	ν_c
366	7.81	3.41 Kc/sec.
374	6.56	5.48 Kc/sec.
388	1.52	30.48 Kc/sec.
400	0.43	—

TABLE III

Molecular reorientation frequencies for *m*-stable (γ) Hydroquinone

Temperature °K	δ H (gauss)	ν_c
350	8.06	0.8043 Kc/sec.
367	7.50	1.9272 Kc/sec.
370	5.00	6.2199 Kc/sec.
374	1.40	23.8720 Kc/sec.
380	1.00	36.6630 Kc/sec.

Thus with above results it is evident that T_1 is greater for stable Hydroquinone in comparison to meta-stable Hydroquinone. Also for both α-Hydroquinone and γ-Hydroquinone the values of T_1 are reduced with rise of temperature. Most likely this is due to rotation of molecule about the molecular axis. The activation energies for both have been calculated. For α-Hydroquinone it is found to be 5.26 K.cal/mole and for γ-Hydroquinone it is about 13.02 K.cal/mole which is a reasonable value to cross the potential barrier hindering rotation (Muzushima 1954). Furthermore, as obtained by Gupta (1963) the second moments and line-widths in both α- and γ-Hydroquinone show a remarkable reduction in its values with the rise of temperature, giving added support to the theory of molecular rotation.

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